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## LIGHT LOSSES IN SOL – GEL COATINGS

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It is shown that the translucence of a substrate strongly influences light transmission by glass articles modified by sol – gel coatings. In contrast to glass, where light scattering is proportional to the refractive index, an inverse proportionality has been found in the films studied, which can be explained by the influence of porosity on the decrease of the refractive index of the coating.

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The conventional method for imparting to glass the required operational properties is to introduce additional components to adjust the composition. This method is used because of the high material costs and requires serious rearrangement of the operative equipment and technology used for production. A more advanced and cheaper method is to change the composition and properties of the surface layer of the glass by depositing thin coatings. This method has found wide application in the production of architectural – construction sheet low-emissivity, self-cleaning, light-protective, and other glasses.

The simplest and cheapest method for depositing coatings is gluing a polymer film on colorless glass. The article obtained acquires light-protective properties but only for a short time because of the low mechanical strength of the polymer. Physical methods (electrochemical and vacuum deposition) are used to obtain “soft” metal and metal – oxide films, imparting useful properties to glass, but the articles require careful handling because of the inadequate strength of the coating. In addition, physical methods are energy intensive and they require expensive equipment.

“Hard” films with the best mechanical properties are deposited chemically. One chemical method — sol – gel technology — is easy to implement, accessible, and inexpensive and at the same time it yields films with maximum strength and diverse properties. The film forming solution (FFS), containing all required oxides and a low-boiling solvent, is deposited on the surface of glass heated approximately up to 400°C or on cold glass. In the latter case the film is secured by brief annealing at low temperature. The sol – gel technology is used to obtain antireflective, decorative, electrically conducting, heat reflecting, and tempered glasses.

The main characteristics of glass as a material for filling translucent panels in buildings and structures are as follows: light transmission, reflection, and scattering. Consequently, the optical properties of sheet glass modified by three-component sol – gel coatings of the system  $\text{Bi}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{TiO}_2$  have now been studied. The iron oxide molar content in these coatings was held constant at 25%, the bismuth oxide content was varied from 10 to 70%, and the titanium oxide content was varied, correspondingly, from 65 to 5%. Bilateral films were deposited by immersion in FFS of samples of thermally polished sheet glass and secured by annealing for 30 min at 450°C.

The viscosity of FFS was measured, the article with a film was monitored according to the coefficient of total light transmission  $T$  (IF-94 apparatus), the spectral coefficient of transmission  $T_\lambda$ , and the mirror reflection  $R$  (Pul’sar spectrophotometer), and the index of refraction  $n$  (LÉf-3M1 ellipsometer), and profilographic analysis of the surface of the coated glass was performed. All measurements and determinations characterizing the coating were performed on the glass side in contact with a protective gas atmosphere of the tin tank during production. To assess the structural – phase transformations in the film material, the modified articles were photographed with magnifications  $\times 100$  (MIM-8M light microscope) and  $\times 10,000$  (UÉMV-100K electron microscope) and x-ray phase analysis of the powders, obtained from the corresponding FFS as described in [1], was performed.

When a light beam with intensity  $I_0$ , taken as 100%, is incident on a glass plate a part  $R$  of the beam is reflected from the glass – air interface, a part  $\varepsilon$  is absorbed by  $d$  elements contaminating or specially introduced into the glass, a part  $r$  is scattered by fluctuations of the glass structure, and the rest  $T$  passes through the glass:

$$I_0 = T + (R + r + \varepsilon).$$

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The coefficient of reflection  $R$  is directly related with the refractive index  $n$  and for a glass free of film is calculated according to the formula [2]

$$R = \frac{n^2 - 1}{n^2 + 1}.$$

The absorption index of glass equals the sum of the products of the specific absorption index of each ion of the  $d$  element  $\chi_{\lambda,i}$  by its mass content  $c_i$  in the glass [3]:

$$\varepsilon = \sum \chi_{\lambda,i} c_i.$$

The scattering is determined by the composition and nonuniformity of the glass at the microscopic level. For silicate glasses the scattering index is determined by fluctuations of the microstructure and is proportional to the refractive index of the glass [3].

The relative closeness of the nature of glass and an oxide sol – gel film [4] permits tentatively extending the laws described above to thin coatings. The mechanism of light losses in glass articles modified by a functional film is much more complicated because of the presence of an additional interface (coating – substrate), and during deposition and heat treatment the coating and glass substrate mutually diffuse, creating a transitional layer [5].

Considering the small thickness of the coating (from 100 Å to 1 μm) as compared with the glass substrate (4 – 6 mm or more), it can be expected with confidence that the light transmission of the substrate will have a large effect on the transmission of light by the modified article. Figure 1 shows the effect of a glass substrate on the index of refraction of samples coated with sol – gel films with the same composition and thickness. The absorption index of glass with thickness  $l$  is defined as follows [2]:

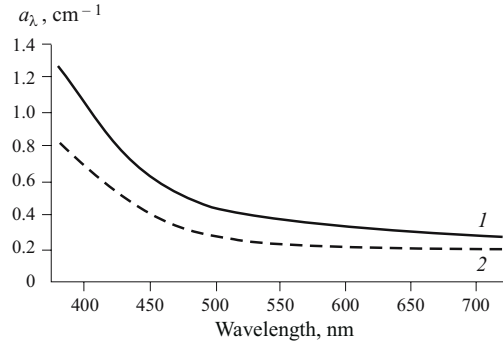
$$a_{\lambda} = \frac{-\lg T_{\lambda}}{l},$$

where  $T_{\lambda}$  is the coefficient of light transmission of the sample.

It is natural for the curve 1 to lie above the curve 2. The measured total coefficients of absorption for samples 1 and 2 with thickness 1 cm equal 57.6 and 49.0%, respectively. This is explained by the difference in the light transmission of the initial glass substrates: 80.9 and 76.5%, respectively.

Therefore, the translucence of the initial glass has a large effect on the transmission of light by modified articles. Consequently, in what follows, to eliminate the influence of the glass substrate on light losses, the film was deposited on a samples cut from a single large piece of sheet glass.

If a film with different composition is deposited on samples with the same spectral coefficients of light transmission, determined by the concentration of coloring impurities in the initial glass and the degree of surface preparation, then the difference  $100 - T - R = X$  at a specific wavelength  $\lambda$  is the sum of the losses due to scattering from the coating – air interface, the absorption due to coloring impurities in the film,



**Fig. 1.** Spectral curve of the absorption index  $a_{\lambda}$  of articles modified by films with the same composition and thickness. The total coefficients of absorption of the samples 1 and 2 (curves 1 and 2) for a thickness of 1 cm equal, respectively, 57.6 and 49.0%.

and scattering by structural nonuniformities (inclusions) in the film. If the number of coloring elements in all coatings is constant, then the losses due to intrinsic absorption are close in all films. Then, the indicated difference  $X$  will depend on the roughness of the surface, determined by the coefficient of diffuse reflection  $R_{\text{dif}}$  or according to the character of the profilogram and the degree of structural nonuniformity of the coating, which can be estimated from photomicrographs and XPA data.

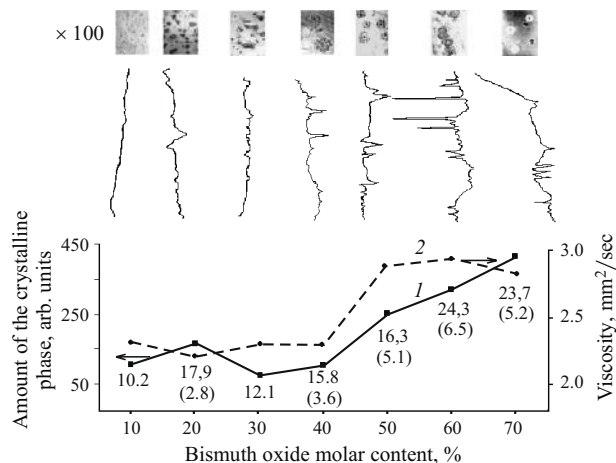
Table 1 gives the molar content of oxides and certain properties of the films studied. The value of  $X$  was calculated according to the expression

$$X = 100 - R_{\text{max}} - T_{\lambda, \text{max}}, \quad (1),$$

where  $R_{\text{max}}$  is the maximum value of the coefficient of mirror reflection, %, and  $T_{\lambda, \text{max}}$  is the light transmission of a film-coated sample at a wavelength corresponding to the maximum value of the coefficient of mirror reflection, %.

When FFS is deposited by immersion, the sol particles move in a laminar flow parallel to the glass plate, which promotes a regular packing of the particles. However close the packing, gaps remain between the vertical and horizontal layers of these spherical particles, and the size of these gaps is proportional to the diameter of the particles. After annealing, gaps continue to exist in the form of pores, penetrating a thin film and filled with air, water vapor, residues of products decomposition and evaporation of FFS components, and so forth. Since, on the one hand nonuniformities in a coating are established when the sol is prepared [6] while on the other hand they are a source of light scattering, the viscosity of FFS, the results of the XPA of powders, and the profilograms and photomicrographs of the films must all be related with one another in a definite manner (Fig. 2).

Since the total light scattering  $X$  in a thin film includes scattering by surface roughness, a direct proportionality should exist between the scattering calculated using the expression (1), the character of the profilograms, and the measured value of the coefficient of diffuse reflection of the



**Fig. 2.** FFS viscosity (1) and amount of the crystalline phase in the powder (2) versus the molar content of bismuth oxide in the coating. The numbers on the curves denote scattering by the films (%) (no parentheses) and the maximum value of the coefficient of diffuse reflection (%) (enclosed in parentheses). Photomicrographs and profilograms of the films are shown at the top of the figure.

films. Such a relation is indeed seen in Fig. 2 for compositions with molar content 40 – 70%  $\text{Bi}_2\text{O}_3$ .

Another component of  $X$  is formed as a result of light scattering by nonuniformities of the microstructure. As already mentioned, light scattering in glass, whose amorphous nature is close to that of the coating, is proportional to the refractive index of the glass. Therefore, the refractive index serves as a criterion for predicting the refractive index of the glass. In contrast to glass, the refractive index  $n_{\text{eff}}$  of a porous body, such as a film, is a complex superposition of the refractive indices of the “framework” of the coating and substances filling the pores; it is described by the expression [7]

$$n_{\text{eff}} = n_1 - \text{Por} (n_1 - n_3) - (n_2 - n_3) f(P/P_0), \quad (2)$$

where  $n_1$ ,  $n_2$ , and  $n_3$  are the refractive indices of the material comprising the “framework” of the layer, adsorbed water,

and air, respectively,  $\text{Por}$  is the porosity, and  $f(P/P_0)$  is the adsorption isotherm written in a general form.

In reality, for a thin coating the expression (2) will be somewhat more complicated because of the probability that the pores will be filled by residues of products decomposition and evaporation of FFS components. Therefore, the higher the film porosity, the more the refractive index of the film will decrease.

Light is scattered in glass by density fluctuations of the material. These fluctuations are expressed much more strongly in thin films, since solid highly reflecting nanoparticles of the “framework” of the film and pores which penetrate the coating and are filled with low-reflecting gaseous substances participate in their formation. The structure of the “framework” of the films can be approximately determined from electron photomicrographs of the films, but it is impossible to measure reliably the refractive index of the particles comprising the “framework” of a coating because there are no instruments and procedures for doing so. In the first, very rough, approximation the value of  $n$  for the “framework” of the film of the experimental system will probably be proportional to the concentration of the most highly refracting component — bismuth oxide.

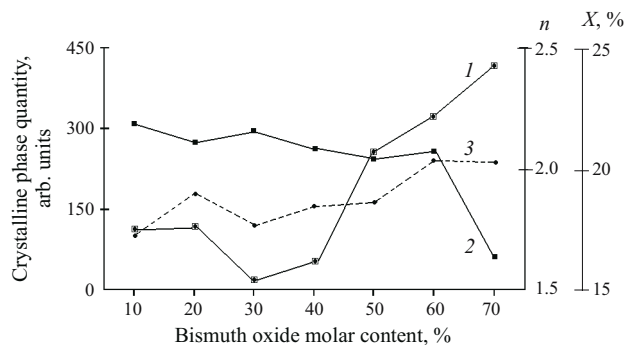
Figure 3 shows the bismuth oxide concentration dependence of the microstructure, refractive index, and light scattering of a coating as well as the concentration of the bismuth-containing component in the powders obtained from the corresponding FFS. As the  $\text{Bi}_2\text{O}_3$  content increases systematically, the quantity of  $\text{BiOCl}$  in the powders changes nonmonotonically, reaching a minimum in a coating containing 30% bismuth oxide. It can be assumed by analogy with glass that the composition named is closer to the phase boundary of the equilibrium diagram of the system  $\text{Bi}_2\text{O}_3 - \text{Fe}_2\text{O}_3 - \text{TiO}_2$  [3].

The change in the structure of the coating supports this assumption. Visually, there are many fewer macro- (see photograph in Fig. 2) and microinclusions in a film with 30% bismuth oxide. This result is all the more important, since the

**TABLE 1.**

Composition	Molar content* of $\text{Bi}_2\text{O}_3$ in the film, %	FFS properties		Confidence interval of the distribution of the properties of coated articles		$T$ , % (for 1 cm thickness)	Scattering $X$ , %
		age, days	viscosity, $\text{mm}^2/\text{sec}$	$n$	$R$ , %		
1	10	16	2.31	2.21 – 2.18	42.3 – 41.1	35.4	10.2
2	20	16	2.23	2.15 – 2.09	35.1 – 34.8	41.9	17.9
3	30	2	2.28	2.20 – 2.17	39.4 – 37.8	36.2	12.1
4	40	2	2.30	2.12 – 2.07	34.5 – 34.3	39.9	15.8
5	50	2	2.85	2.09 – 2.00	31.9 – 30.5	45.7	16.3
6	60	2	2.88	2.23 – 1.92	29.5 – 29.3	43.1	24.3
7	70	2	2.80	1.73 – 1.55	21.7 – 21.1	59.7	23.7

\* The molar content of iron oxide is constant and equals 25%; the content of  $\text{TiO}_2$  changes from 65 to 5% on changing from composition 1 to composition 7.



**Fig. 3.** Quantity of the crystalline phase  $\text{BiOCl}$  (1) and the average values of the refractive index  $n$  of the coating (2) and scattering index  $X$  (3) versus the bismuth oxide molar content.

three-component phase diagram named above has not been studied. The curves 1 and 3 in Fig. 3 have almost the same variation, which confirms the reality of the contribution of the nature and refractive index of the “framework” particles to light scattering of thin films. An increase of the concentration of the highly refracting phase in the “framework” should result in a higher index of refraction of the film. However, comparing curves 1 and 2 (see Fig. 3) indicates that these quantities are inversely proportional to one another. This can be explained by an increase in the porosity of the coating as the film becomes enriched with bismuth oxide. Therefore, as the  $\text{Bi}_2\text{O}_3$  content increases, the fluctuations occurring in the film intensify because of an increase in the content of the strongly refracting oxide in the “framework” on the one hand and an increase in the concentration of pores filled with weakly refracting gaseous products on the other. This should increase the light scattering (see Fig. 3, curve 3). Consequently, the measure refractive index of the coating cannot

serve as a reliable criterion for predicting the expected light scattering in an article modified by a thin film.

In summary, the translucence of an initial glass – substrate has a strong effect on light transmission by modified articles.

The total light scattering in a thin film includes scattering by surface roughness, which is confirmed by the existence of direct proportionality between the computed magnitude of scattering, the character of the profilograms, and the measured coefficient of diffuse reflection of the films.

In contrast to glass where light scattering is proportional to the refractive index, an inverse proportionality was found in the films studied. This can be explained by the influence of porosity of the coating on the decrease of its refractive index.

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